Read Me: UNIFAC-FV

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UNIFAC-FV Overview

UNIFAC also known as Universal functional-group activity coefficient, is a method to predict the activity of systems.[1] This method consists of two parts, the combinatorial and the residual part. These contributions to the overall activity are shown in Eqn. 1

$$\ln(a_1) = \ln\left(a_1^C\right) + \ln\left(a_1^R\right) \tag{1}$$

Where:

a_1 is the activity of the solvent in the binary mixture

a_1^C is the combinatorial contribution to the total activity

a_1^R is the residual contribution to the total activity

Combinatorial

The combinatorial part takes into account the activity contribution due to differences in size and shape of the molecules.

$$\begin{aligned} \ln\left(a_1^C\right) &= \ln(\phi_1') + \phi_2\left(1 - \frac{1}{m}\right) \\ &+ \frac{z}{2} M_1 q_1' \ln\left(\frac{\theta_1'}{\phi_1'}\right) - \frac{z}{2} M_1 q_1' \ln\left(1 - \frac{\theta_1'}{\phi_1'}\right) \end{aligned} \tag{2}$$

Where:

z is the coordination number which is fixed to 10. It represents the number of close interacting molecules around a central molecule. For spherical cubic packing, z = 6, for hexagonal packing, z = 12. z = 10 is often chosen as an intermediary value between these two types of packing.[2]

M_1 is the molecular weight of solvent

ϕ_i' is the segment fraction, which is a composition variable, described in Eqn. 3

θ_i' is the surface fraction, which is a composition variable, described in Eqn. 4

q_i' is the sum of group area parameter divided by molecular weight, described in Eqn. 5

$$\phi_i' = \frac{r_i' w_i}{\sum_j r_j' w_j} \tag{3}$$

Where:

w_i is the weight fraction of i (which can be the polymer (1) or the solvent (2))

r_i' is the parameter related to molar group volume, described in Eqn. 6

$$\theta_i' = \frac{q_i' w_i}{\sum_j q_j' w_j} \tag{4}$$

$$q_i' = \frac{1}{M_i} \sum_k v_k^{(i)} Q_k \tag{5}$$

Where:

$v_k^{(i)}$ is the number of subgroups of type k in molecule i

Q_k is the group area parameter, obtained from normalizing the Van der Waals surface area by a -CH_2- group in polypropylene, as described by Eqn. 7

$$r_i' = \frac{1}{M_i} \sum_k v_k^{(i)} R_k \tag{6}$$

Where:

R_k: molar group volume, obtained from normalizing the Van Der Waals group volume by a -CH_2- group in polyethylene, as described by Eqn. 8

$$Q_k = \frac{A_{wk}}{2.9 \times 10^9} \tag{7}$$

Where:

A_{wk} is the Van der Waals group surface area

2.9×10^9 is the Van der Waals group surface area of a -CH_2- group in polyethylene

$$R_k = \frac{V_{wk}}{15.17} \tag{8}$$

Where:

V_{wk} is the Van der Waals group volume

15.17 is the Van der Waals group volume of a -CH_2- group in polyethylene.

Residual

The residual part takes into account the energy interactions, functional group sizes, and interaction surface areas, as described by Eqn. 9.

$$\ln\left(a_1^R\right) = \sum_k v_k^{(i)} \left[\ln(\Gamma_k) - \ln\left(\Gamma_k^{(i)}\right)\right] \tag{9}$$

Where:

Γ_k is the group residual activity of group k, as described in Eqn. 10

$\Gamma_k^{(i)}$ is the group residual activity of group k in a reference solution containing only molecules of type i, this is done to attain the normalization that a_1 approaches 1 as w_1 approaches 1, and is described in Eqn. 10

$$\ln(\Gamma_k) = M_k Q'_k \left[1 - \ln\left(\sum_m \Theta'_m \psi_{mk}\right) - \sum_m \left(\frac{\Theta'_m \psi_{km}}{\sum_n \Theta'_n \psi_{nm}}\right)\right] \tag{10}$$

Where:

Θ'_m is the area fraction of group m, over the sums of the area fraction of all different groups as described by Eqn. 11. Note that this is slightly different from θ'_i, which is the surface fraction described in Eqn. 4

ψ_{mk} is the group interaction parameter as described in Eqn. 14

$$\Theta'_m = \frac{Q'_m W_m}{\sum_n Q'_n W_n} = \Theta_m \tag{11}$$

Where:

Q'_m is the group area parameter divided by the molar mass of that group as shown in Eqn. 12, similar, but not equal to that described in Eqn. 5

W_m is the mole fraction of the subgroup as described in Eqn. 13

$$Q'_m = Q'_k = \frac{Q_k}{M_k} \tag{12}$$

$$W_m = \frac{w_i M_m}{M_i} \tag{13}$$

Where:

M_m is the molar mass of group m which is in molecule i

M_i is the molar mass of molecule i

$$\psi_{mn} = \exp\left[-\left(\frac{U_{mn} - U_{nn}}{RT}\right)\right] = \exp\left[-\left(\frac{a_{mn}}{T}\right)\right] \tag{14}$$

Where:

U_{mn} is the energy of interaction between groups m and n

a_{mn} is the interaction parameter

It is important to note that while the energy of interaction between groups is the same regardless of order, $U_{mn} = U_{nm}$, the same does not hold for the interaction parameter, a_{mn}. $a_{mn} \neq a_{nm}$, this is described in Eqn. 15. Another important distinction is that unlike in previous equations these groups are referring to main groups, not subgroups. This is because each subgroup in the main group will have the same interaction parameter, and the interaction between 2 groups that are a part of the same main group is 0, because if

$U_{mn} = U_{nn}$ then $a_{mn} = 0$, as described in Eqn. 15.

$$a_{mn} = \frac{U_{mn} - U_{nn}}{R} \neq a_{nm} = \frac{U_{mn} - U_{mm}}{R} \tag{15}$$

Free Volume

This method works well for most systems with small molecules. However, polymers are quite large, and as such the free volume contribution to the overall activity is significant. Hence, the need for a third term, the free volume.

$$\ln(a_1) = \ln\left(a_1^C\right) + \ln\left(a_1^R\right) + \ln\left(a_1^{FV}\right) \tag{16}$$

$$\ln(a_1^{FV}) = 3c_1 \ln\left[\frac{\bar{v}_1^{1/3} - 1}{\bar{v}_M^{1/3} - 1}\right] - c_1\left[\left(\frac{\bar{v}_1}{\bar{v}_M} - 1\right)\left(1 - \frac{1}{\bar{v}_1^{1/3}}\right)^{-1}\right] \tag{17}$$

Where:

$\bar{v_1}$ is the reduced volume of the solvent, as decribed by Eqn. 18

$\bar{v_M}$ is the reduced volume of the mixture, as decribed by Eqn. 20

$3c_1$ is the number of external degrees of freedom, $c_1 \approx 1.1$ may change depending on solvent (especially for large solvents), this is described in more detail by Gotlieb et. al.,[3] in the python script below we fix this value at 1.1

$$\bar{v_1} = \frac{v_1}{15.17 b r_1'} \tag{18}$$

Where:

v_1 is the volume of solvent per gram, as described by Eqn. 19

15.17 is the Van der Waals group volume of a unit of -CH_2- in polypropylene, this is multiplied with r_1' to undo the normalization described in eqns. 8 and 6

b is the proportional factor of order unity, which is an empirical parameter similar to c_1 which Oishi and Prausnitz recommend be fixed at 1.28. However, as is noted by Eqn. 18, if

the volume of the solvent, v_1, is less than $b = 1.28$ times the hardcore volume of the solvent, which is $15.17r_1'$, then the reduced volume will be less than 1, leading to a negative in the logarithm shown in Eqn. 16. This is a known problem with this method. One solution is described by Seiler et al. is to simply set the b parameter equal to 1 in the event that this occurs[4]

$$v_1 = \frac{1}{\rho_1} \tag{19}$$

Where:

ρ_1 is the density of the solvent

$$\bar{v}_M = \frac{v_1 w_1 + v_2 w_2}{15.17b(r_1' w_1 + r_2' w_2)} \tag{20}$$

Where:

$\bar{v_M}$ is the reduced volume of mixture per gram, assuming the mixture is additive

v_2 is the volume per gram polymer as described by Eqn. 21

21

$$v_2 = \frac{1}{\rho_2} \tag{21}$$

Where:

ρ_2 is the density of the polymer

Parameters

UNIFAC-FV is a group method, as such the size and shape are pure-component group parameters. These parameters are the Van der Waals group volume and surface area, these are determined for each subgroup. The energy contributions are determined from VLE data, for each main group. To better illustrate this idea we can think of a simple example of the solvent Octane and the polymer polypropylene.

Octane is composed of 2 subgroups, CH_3 and CH_2. These subgroups appear in different

amounts in Octane, there are 2 CH_3 and 6 CH_2. In UNIFAC-FV notation, this would be $v_{CH_3}^{(Solvent)} = v_1^{(2)} = 2$ and $v_{CH_2}^{(Solvent)} = v_2^{(2)} = 6$. Each of these subgroups has a Van der Waals group volume, V_{wk}, and Van der Waals group area, A_{wk}, which can be found in literature.

For polymers, in this example, polypropylene, we define the polymer by their monomer and the degree of polymerization (the number of monomers in the overall polymer). It is important to note that UNIFAC-FV, does not use the degree of polymerization as an input, it calculates the activity from the interactions between a monomer and the solvent. A monomer of polypropylene contains 3 subgroups CH_3, CH_2, and CH. These subgroups appear in different amounts in polypropylene, there is 1 CH_3, 1 CH_2, and 1 CH. In UNIFAC-FV notation, this would be $v_{CH_3}^{(Polymer)} = v_1^{(1)} = 1$, $v_{CH_2}^{(Polymer)} = v_2^{(1)} = 1$, and $v_{CH}^{(Polymer)} = v_3^{(1)} = 1$. Each of these subgroups has a Van der Waals group volume, V_{wk}, and Van der Waals group area, A_{wk}, which can be found in the literature. Because we are describing group parameters they are the same regardless of the molecule. In other words, the CH_3 group in Octane will have the same parameters as the CH_3 group in a monomer of polypropylene.

The interaction parameter, a_{mn} is determined between main groups. CH_3, CH_2, CH, and C all belong to main group 1, since they belong to the same main group the interaction energy between them will be 0. In this case, since all of our subgroups for both the polymer and the solvent are in the same main group the interaction parameters are all 0. These interaction parameters are determined by VLE data and can be found in the literature. Because this interaction parameter occurs between each subgroup and every other group it is best described as a 2D array.

Interaction parameters between different subgroups.

Name [subgroup k]	CH3 [1]	CH2 [2]	CH [3]
CH3 [1]	0	0	0
CH2 [2]	0	0	0
CH [3]	0	0	0

TABLE 2: Since interaction parameters are calculated between main groups, it is clearer to make the tables dependent on the main group(s).

Name [main group m]	CH3 [1]	CH2 [1]	CH [1]
CH3 [1]	0	0	0
CH2 [1]	0	0	0
CH [1]	0	0	0

Flory-Huggins Parameter

A python script was developed to calculate UNIFAC-FV activities, and then fitting those activities to the Flory-Huggins equation 22 to obtain the Flory-Huggins interaction parameter as derived in the Brandup et. al. Polymer Handbook (Eq. D6 in Ch. VII/247 Polymer-solvent Interaction Parameters)[5] .

$$\ln(a_1) = \ln(1-\phi_2) + \left(1 - \frac{1}{N}\right)\phi_2 + \chi\phi_2^2 \tag{22}$$

Where:

a_1 is the solvent activity calculated from UNIFAC-FV

ϕ_2 is the volume fraction of the polymer

N is the degree of polymerization

χ is the Flory-Huggins interaction parameter

The inputs into this python script are all the inputs into UNIFAC-FV described in section 1, in addition to the degree of polymerization N and the temperature. However, the pure-component group parameters, like R_k, Q_k, k, m, and molar mass are automatically found from an attached database for most groups. The interaction parameter is similarly, automatically found from an attached database. Allowing for less inputs to be needed. Note: By default the solvent mass fraction array is set equal to 0.09575, 0.05, 0.02, 0.01, 0.001, 0.00001.

Using the Python Script for UNIFAC-FV

Important: All files should be present in the same folder. This includes the "Functions.ipynb" file, which should be run first. The "Widgets.ipynb" file, "Parameters.xlsx", and "Components.xlsx". If you wish to use input files for calculations rather than using the GUI provided, those files should similarly be in the same folder.

Note: If you modify the "Functions.ipynb" file in any way, you should re-start the kernel, clear outputs, re-run the "Functions.ipynb" file, and then repeat the procedure for the "Widgets.ipynb" file. If this is not done, the modifications will likely have no effect (or worse, unintended effects).

It is important to note that the parameters, used here in the "Parameters.xlsx" are from a **database**, except for the carbonate parameters, those were obtained from Yunjn and Junming.[6]

We can define the new inputs in code as seen below:

```
# ACETONE
name_k_ACN = ['CH3', 'CH3CO'] # MAKE SURE NAMES ARE CORRECT CH3CO =/= COCH3
vk_ACN = [1, 1]
rho_S_ACN = 0.791 # density (g/cm^3)

# POLYPROPYLENE
name_p = ['CH3', 'CH2', 'CH']
vk_p = [1, 1, 1]
rho_P_ACN = 0.865 # density (g/cm^3)
DP = 2000/42 # Degree of polymerization = number of monomers per polymer molecule

T = 25 + 273.15 # K
```

FIGURE 1: A fragment of Python code defining the parameters used in the UNIFAC-FV calculation.

Here we describe the names of each of the groups (name_P) and (name_S). The amount of each subgroup present in the monomer and solvent (vk_P) and (vk_S. The degree of polymerization (DP), as shown above it is found from the overall molecular weight of the polymer (2000 g/mol) divided by the molecular weight of the monomer (42 g/mol). The densities of the polymer and solvent (rho_P) and (rho_S). The overall temperature (T).

This can also be inputted into an interactive interface (Jupyter Widget).

FIGURE 2: Here we can select the method we will use "UNIFAC-FV" or "UNIFAC".

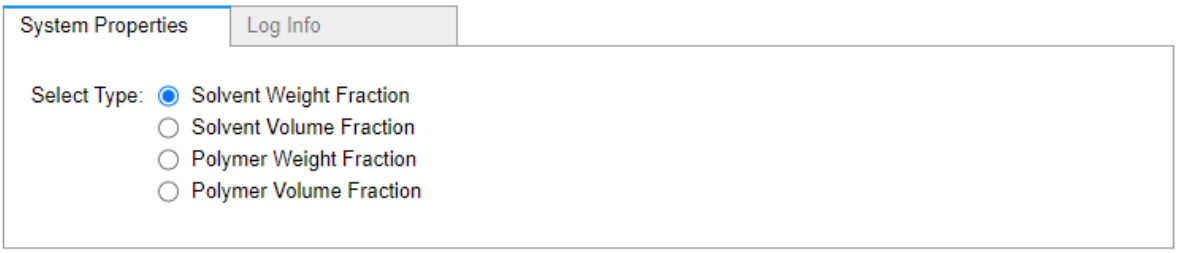

FIGURE 3: Here we can select how we are planning to define the fractions inputted into the system. We can choose from 4 different basis, shown above.

FIGURE 4: Here we can change the name of the log file that will be outputted when UNIFAC-FV runs.

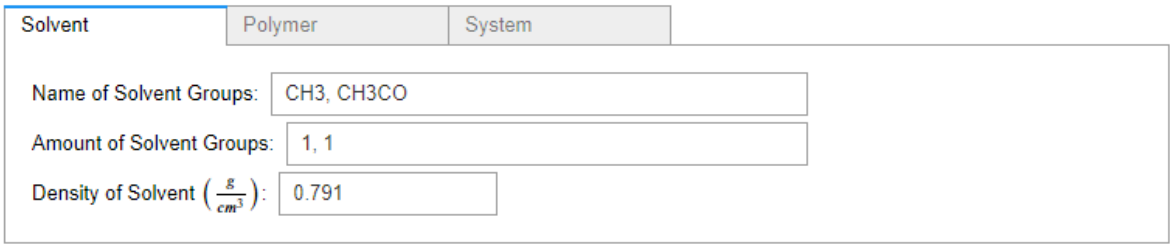

FIGURE 5: Here we can type in the parameters to define the Solvent.

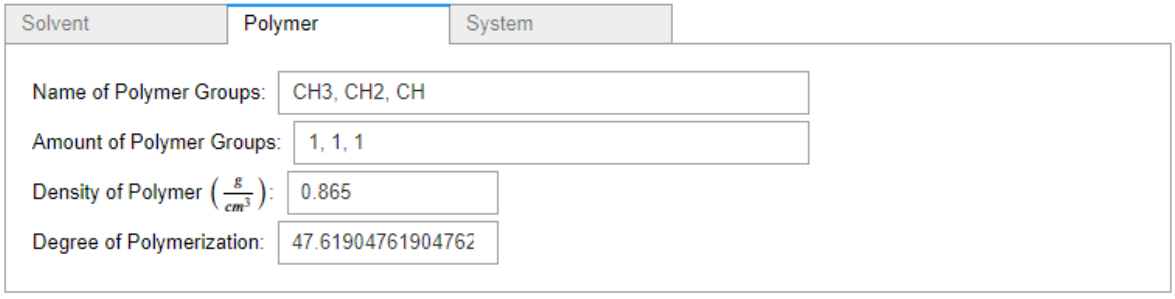

FIGURE 6: Here we can type in the parameters to define the Polymer.

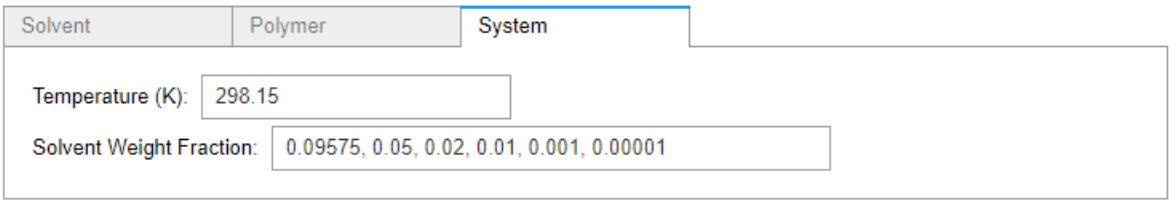

FIGURE 7: Here we can type in the parameters to define the System temperature, and here we can define the fractions in terms of the basis defined above. In this case, the Solvent Weight Fraction.

```
         k      Rk     Qk  V_k^(1)  V_k^(2)
CH3      1  0.9011  0.848        1        1
CH2      2  0.6744  0.540        0        1
CH       3  0.4469  0.228        0        1
CH3CO   18  1.6724  1.488        1        0

[[  0.     0.     0.   476.4 ]
 [  0.     0.     0.   476.4 ]
 [  0.     0.     0.   476.4 ]
 [ 26.76  26.76  26.76   0.  ]]

a (b = 1 or 1.28 depending on hard core volume)
[1.16392240e+00 8.56014912e-01 4.43137600e-01 2.43151842e-01
 2.65250030e-02 2.67854256e-04]

vol_frac2
[0.89622196 0.94557695 0.9781698  0.9890747  0.99890655 0.99998906]

_____________________________________________
Flory-Huggins Parameter: 1.985144772001753 4
_____________________________________________
```

FIGURE 8: This is the output to the script.

The output will list the different solvent inputs, make a table summary of some of the input parameters and display the interaction parameters found from the database. This allows for verification (in the event that the database is wrong or if there was a typo in the inputs). Display the activities (using Seiler et. al.[4] b parameter), the volume fraction of the polymer, and the corresponding Flory-Huggins Interaction parameter calculated from fitting those activities and Volume Fraction with Eqn. 22.

An alternative input method is using the input files. For inputting information for a UNIFAC-FV calculation, the input file should have the file extension '.UFVinp'.

```
Solvent: Perfluorooctane
Polymer: Polypropylene
Solvent Density (g/cm3): 0.897
Polymer Density (g/cm3): 0.865
Degree of Polymerization: 47.62
Temperature (K): 298.15
Type: Solvent Weight
Fraction: 0.09575, 0.05, 0.02, 0.01, 0.001, 0.00001
```

FIGURE 9: This is the input file to the UNIFAC-FV script.

Here we can see the Solvent and Polymer being defined. Note: If you wish to add a new Solvent or Polymer please modify the "Components.xlsx" file. This file contains a list of the subgroups and subgroup amounts associated with each component name. Next we define the density of the solvent and polymer, please note the units. We also define the degree of polymerization, the temperature and the basis for our fractions, which is defined in the last line.

To run a UNIFAC calculation, simply us the file extension '.Uinp'. By running the function 'Read_Input()', python will automatically find all files in the folder with these file extensions and run the calculations. The results will be placed in the '.UFVlog' and '.Ulog' files respectively.

```
Mixture: 2
Component 1: Diethylamine
Mole Fraction 1: 0.4, 0.5, 0.6
Component 2: Heptane
Mole Fraction 2: 0.6, 0.5, 0.4
Temperature (K): 308.15
```

FIGURE 10: This is the input file to the UNIFAC script.

Here we can see the number of components being listed, in this case only 2. Then we can see that for each component we define the name and its mole fraction, and the overall system temperature.

Note: If you wish to add a new Component please modify the solvents section of the "Components.xlsx" file. This file contains a list of the subgroups and subgroup amounts associated with each component name.

Note: There is no limit to the number of components you can have, 2 was just used in this example.

```
Polymer Name: Polypropylene
Polymer Density (g/cm^3): 0.865
Solvent Name: Perfluorooctane
Solvent Density (g/cm^3): 0.897
Degree of Polymerization: 47.62
Temperature (K): 298.15
Solvent Weight: [9.575e-02 5.000e-02 2.000e-02 1.000e-02 1.000e-03 1.000e-05]
Activities: [5.36982678e+00 3.67807776e+00 1.77824323e+00 9.49365070e-01
 1.00818904e-01 1.01494607e-03]
Flory-Huggins Parameter: 3.8
Exited with no errors or warnings.
```

FIGURE 11: This is the output file to the UNIFAC-FV script.

Here we can see the output file for UNIFAC-FV. Note that the file name is equivalent to the input file name, with a different extension '.UFVlog'. We can see that it summarizes the inputs, then it also returns the activities, and the Flory-Huggins parameter.

```
For Diethylamine:
Mole Fraction: [0.4 0.5 0.6]
Activity Coefficient: [1.133 1.094 1.062]

For Heptane:
Mole Fraction: [0.6 0.5 0.4]
Activity Coefficient: [1.047 1.077 1.118]

Exited with no errors or warnings.
```

FIGURE 12: This is the output file to the UNIFAC script.

Here we can see the output file for UNIFAC. Note that the file name is equivalent to the input file name, with a different extension '.Ulog'. We can see that it summarizes the inputs, then it also returns the activity coefficients. It is important to note that activity is **not** the

same as activity coefficient.

References

(1) Oishi, T.; Prausnitz, J. M. Estimation of solvent activities in polymer solutions using a group-contribution method. *Industrial & Engineering Chemistry Process Design and Development* **1978**, *17*, 333–339.

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(3) Gottlieb, M.; Herskowitz, M. External-degrees-of-freedom parameter in the UNIFAC-FV model. Comments. *Industrial & Engineering Chemistry Process Design and Development* **1982**, *21*, 536–537.

(4) Seiler, M.; Rolker, J.; Mokrushina, L.; Kautz, H.; Frey, H.; Arlt, W. Vapor–liquid equilibria in dendrimer and hyperbranched polymer solutions: experimental data and modeling using UNIFAC-FV. *Fluid phase equilibria* **2004**, *221*, 83–96.

(5) Brandup, J., et al. Polymer Handbook 4th Edition John Wiley & Sons. *Inc. New York* **1999**,

(6) Yunjin, F.; Junming, Q. Estimation and Test of Interaction Parameters in the UNIFAC Model of Group—OCOO—with Group—CH3, ACH, CH3OH and CH3COO—. *Chinese Journal of Chemical Engineering* **2005**, *13*, 271–275.